Synthesis of the string-like CNT having few layer stacking of graphene

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ABSTRACT

In this study, raw material calcined and cobalt acetylacetonato were mixed with 2-methoxyethanol solution and then dried it. After its treatment, obtained sample which cobalt was loaded on surface of raw material calcined was treated under Ar atmosphere at high pressure. H_2 and CH_4 generated from raw material calcined derived the graphene without catalyst, however, in the case of loading the cobalt as catalyst, CNT has abundantly generated through working of catalyst. Stacking of the graphene in CNT was suppressed under high pressure of Ar, as a consequence, synthesized CNT having thin wall and large external diameter mutually bounded under atmospheric pressure by the van der Waals force, and then flexible and strings (flat-circle) form CNT was synthesized. Its CNT uniformly-dispersed in liquid without fomation of boudle.

Therefore, CNT obtained in this process might be expected the application of transparent conductive film through wet coating process as conductive pass formation material. This CNT having interesting morphology will be expected to the application of drug delivery system.

Keywords: single wall carbon nanotube (SWCNT), multi wall carbon nanotube(MWCNT), few layer graphene, thin-walled carbon nanotube, transparent conductive film, drag delivery system

1 INTRODUCTION

Carbon nanotube has been classified into Multi wall carbon nanotube (MWCNT) and Single wall carbon nanotube (SWCNT), and development for the practical application is carried out in each area such as electronics and mechanical field. MWCNT is used as electroconductive filler for tray of the semiconductor carrier and as reinforcement to tennis racket [1]. However, in addition to the price being expensive for the SWCNT, aggregability is high, bundle is easy to be formed, and homogeneous dispersion is inferior, therefore the practical applications have been grew stangnat [2] CNT exhibits ~~manifests~~ excellent electron mobility, thermal conductivity and optical transparency which excel carbon fiber or graphite fiber [3]. It seems to be the graphite on the physical property in MWCNT with stacking number of several decades. Therefore, it is desirable in the CNT that the stacking number of the graphene to which be the basic structure is less than 10 layers [4]. On the other hands, aggregability of each CNT will be heightened with increasing of van der Waals force of CNT itself through decreasing of stacking number of graphene layers. As the results, bundle is formed, and it will be derived that uniform dispersion becomes difficult. In addition it has been indicated that the thinly rigid structure of CNT brings about the health hazard similar to the asbestos [5]. In MWCNT having thickness layer with rigid particularly, its tendency is remarkable. On the other hands, we have succeeded in abundantly formation of the graphene through CVD reaction using calcined resin containing hydrogen moderately through heat-treatment under and high-pressure with isotropic gas pressure [6-8]. In this study and development, it will be discussed in synthesizing of flexible CNT having few layers graphene and showing the excellent physical property different from graphite fibers.

2 EXPERIMENTAL

2.1 Catalyst preparation

Spherical phenol resin was calcined at a temperature less than 1000 °C in a nitrogen gas flow. Amount of hydorgen containig calcined resin was measureed by fusion method using inert gas through high-frequency heating; transferring of the hydrogen gas generated and determing of the amount of its hydrogen gas was carried out thermal conductivity detector (Horiba; EMGA621). Its hydrogen content is 5000 ppm. This calcined resin was mixed with 1wt% cobalt acetylacetonate (Special Grade available from NACALAI TESQUE, NC.,) and methoxyethanol (available from NACALAI TESQUE, INC., purity: 99 %)solution, and this solution containing the calcined resin was filtrated under reduced pressure using an aspirator equipped with a diaphragm pump. Obtained mixture was air-dried in a draft for 24 hours, and then heat treated to 500°C under air to make the Co dispersed on carbon surface.

2.2 CNT growth

Its mixture was put in a crucible with mounting screw and a cap. Its screw was turned to tighten and sealed. Its crucible putting the mixture was charged in a pressure vessel having containing a carbon heater and a heat insulate layer (Fig.1), and then the inside temperature of a heat insulate layer of a pressure vessel increased to 1100 °C at a temperature programing rate 500 °C/h under isostatic pressing at 190 MPa using argon gas. Temperature inner surface of the pressure vessel was maintained below 100°C by the water cooling tube [6-8].

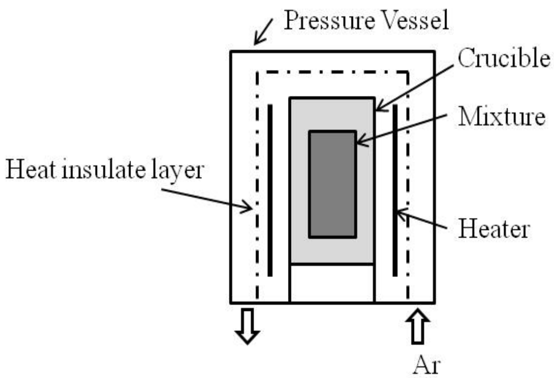

Fig.1 Schematic showing the cross-section of equipment

2.3 Preparation of CNT dispersion

Cobalt remained in obtained CNT was removed by washing in 0.5 mol/dm^3 hydrochloric acid, and then it was treated in the 2-propanol (Wakojunnyakukogyo 99.5% grade) by using ultrasonication for 15minutes with 600W power and 24kHz frequency. After ultrasonication, its solution was separated to the CNT dispersed solution (CNT dispersion) and the residue by centrifugation with 500G. The CNT dispersed solution was filtarated by using a micro-grid. The samples on the micro-grid was analyzed by Raman spectroscopy using a JASCO NRS2100 with 514 nm laser line excitation and 50mw power. Samples were also characterized by scaning microscopy (SEM: Hitachi 5500 and a FEI Sirion), and tranmission electgron microscopy (TEM:Jeol 2010F).

3 RESULTS AND DISCUSSION

A large amount of CNT with nearly circular cross-section morphology having about 40 to about 80 nm in an outer diameter, about 2 to about 3 nm in a thickness and about 10 to about 100μm in a length were generated on the product treated through on this process.

This CNT was characterized by having a thin thickness for its diameter as compared with CNT prepared by conventional method [4], and a ratio of its thickness to the outer diameter was less than 10 %. Fig.2 shows SEM image of CNT as grown in the heat treatment procsess under high Ar gas pressure, and it has unique shape looks like a thin and flat string such as flat circle. Fig. 3 shows a TEM photograph of the CNT obtained, which indicates thickness of the tube wall and the inner diameter measured, respectiverly. Its outer diameter and thickness was 55 nm and 2.2 nm, respectverly and ratio of this thickness to the outer diameter was about 4.0 %.

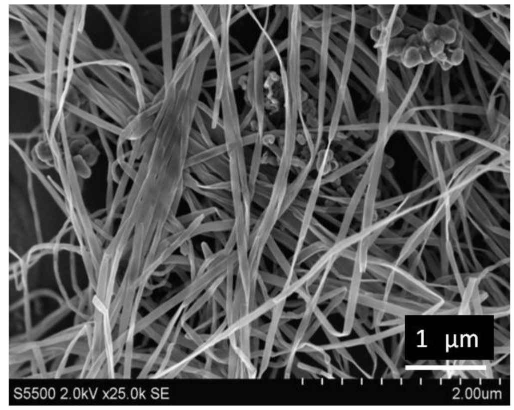

Fig.2 SEM image of CNT grown under high Ar pressure

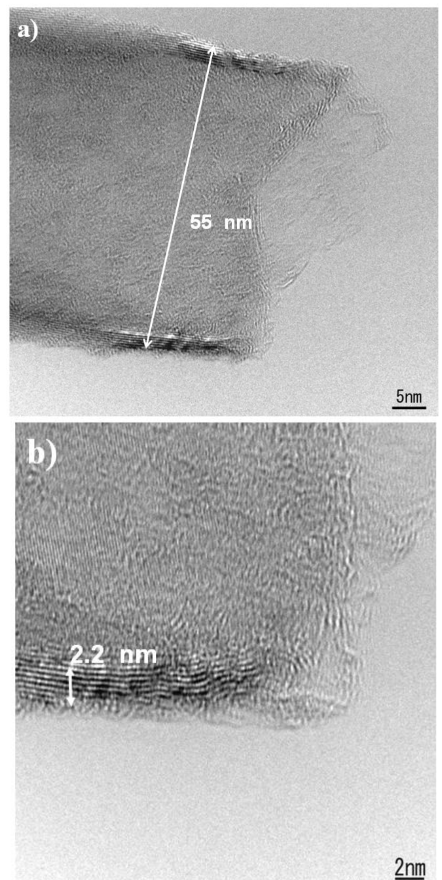

Fig. 3 TEM photograph of the obtained CNT
a)leadeing edge of CNT, b)lattice image of thin wall

This result also indicates morphology of flat circle CNT. A lattice fringe image of TEM photograph is shown that graphene layers stacked in the thickness direction of this CNT. From this photograph, this CNT was build up with graphene stacked 7 layers, and this CNT was also confirmed good crystallinity. There were a strong and sharp peak at 1590 cm^{-1} correspond to G-band, a weak and broad peak around 1350 cm^{-1} correspond to D-band and a peak around 2700 cm^{-1} correspond to 2D-band as shown in Fig.4. The Raman spectroscopy of this sample obtained also shows good crystallinity as same as TEM observation.

In the case of CNT prepared by conventional method, inner diameter also decrease while outer diameter incerease with increase in a number of graphene layers in CNT. However, inside space having this CNT obtained is not changed in spite of increasing in outer diameter.

Inside space of CNT obtained is very wide, therefore, it is considered that it can be used for the flowing of liquid and gas.

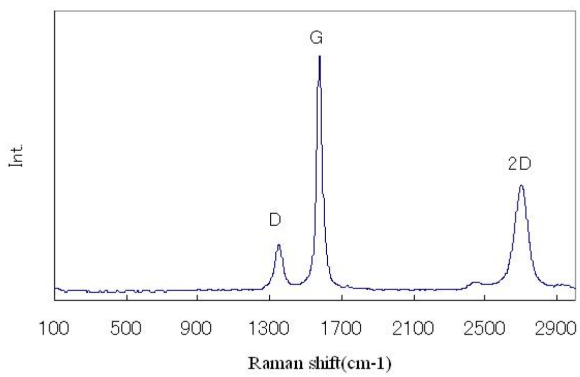

Fig.4 Raman spectroscopy of the obtained CNT

Cui et al reported that thin-walled, open-ended, and well-alligned N-doped CNT were synthesized by using acetonitorile as a carbon source, and then its thin-walled index (defined as the ratio of inner diameter and wall thickness of CNT) was between 2.8 and 6.2 as a average value for each 50 specimens [9].

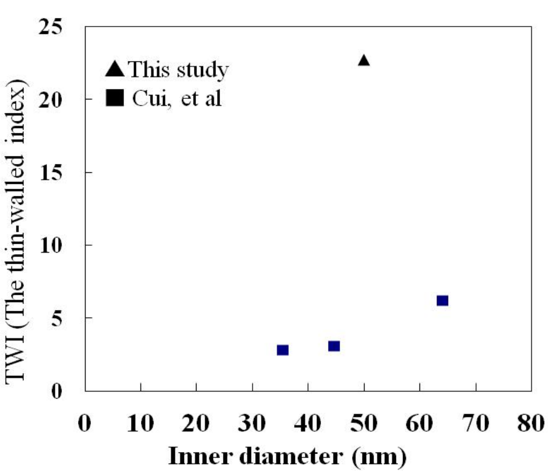

Fig.5 Comparison of TWI for thin-walled CNT

The CNT obtained in this study shows extremely higher thin-walled index in comparison with the thin-walled CNT by Cui et al., as shown in Fig.5. Stacking number of the graphene in CNT was suppressed under high pressure of Ar, as a consequence, extremely thin-walled and 40-80 nm in external diameter was formed.

This CNT having thin wall and large external diameter mutually bounded under atmospheric pressure by the van der Waals force, and the flexible and strings form like the rubber tube of the bicycle in which the air came out was shown in Fig. 2, Fig.3(a) and (b). Its morphology might be compared to flat-circle. This reaction mechanism is proposed in Fig.6. At the bigininng this CNT grows cylindrically and thicker outer diameter, however its diameter will be changed to extremely thin thickness because of high pressure Ar existence. At the end of process with atmospheric pressure, adhesion of inner wall by the Van der Waals force easily occur since the rigidity of thin wall might be small.

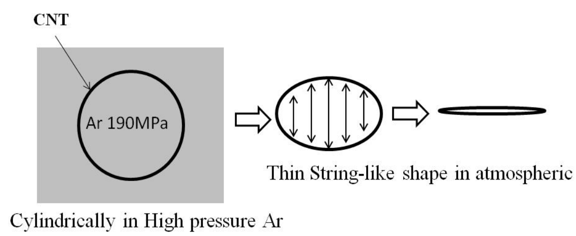

Fig.6 The mechanism of string-like (flat-circle) shape CNT growth

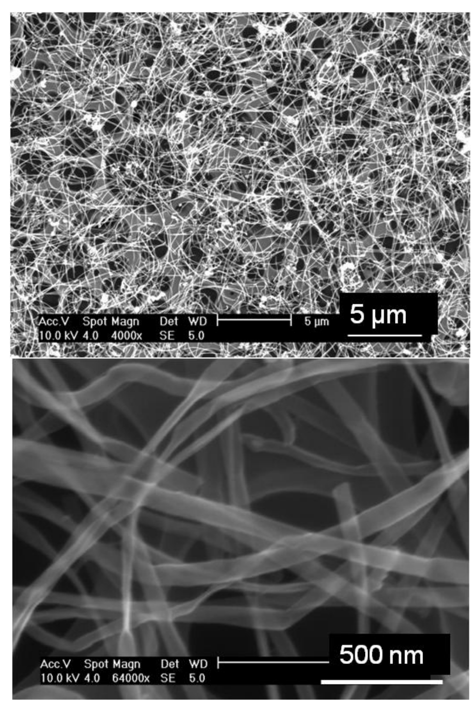

Fig.7 SEM micrographs of flat-cycle CNT (a) low magnification, (b) high miagnification

Obtained CNT could be dispersed in 2- propanol without any surfactant, and the amount of dispersed CNT was 0.1mg/ml. After filtration of its solution by a micro-grid, morphology of its CNT is shown in Fig.7. In this figure, The dispersibility of CNT is good and formation of the remarkable bundle was not recognized.

4. CONCLUSION

String-like (flat circle) CNT having few layers graphene was synthesized under isostatic pressing at 190 MPa using argon gas. In comparison of CNT prepared by conventional method, inside space of CNT obtained is very wide. It also indicated extremely higher thin-walled index in comparison with the thin-walled CNT reported by Cui et. al. Stacking number of the graphene in CNT was suppressed under high pressure of Ar, as a consequence, extremely thin-walled and 40-80 nm in external diameter was formed. It is considered that it can be used for the flowing of liquid and gas.

CNT obtained in this process might be expected the application of transparent conductive film through wet coating process as conductive pass formation material. It might be able to optionally control string (flat-circle) form which tube is hollow and obstruction by using organic solvent. This CNT having interesting morphology will be also expected to the application of drug delivery system. Also graphene layer constructing to this CNT is very good in electron conductivity, and has a possibility for catalytic activity, selective reaction of pharmaceuticals or the like utilizing the graphene surface. Further, in this CNT as a one-dimensionally unified space, a behavior being different from conventional physical and chemical reactions might be anticipated through its effective utilization.

5. REFERENCES

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